STUDIES ON POLYMERIC ELECTROLYTES

BY

EDWARD HERBERT de BUTTS, JR.

B. S., George Washington University, 1943

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
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R. UNIV. BIBLIOTHEEK LEIDEN

STUDIES ON POLYMERIC ELECTROLYTES

Introduction

The thermodynamic properties of simple electrolytes are relatively well understood, but there has been comparatively little research carried out on molecules whose ions are capable of assuming very high charges. These compounds can be designated "polymeric electrolytes" of which polyacrylic acid, polyvinyl amine, and the copolymer of maleic acid and styrene are typical. These substances are soluble in water and undergo the usual acid-base equilibria. Staudinger (1) and Kern (2) (3) describe a number of experiments on aqueous solutions of polyacrylic acid and their salts and report that the properties of these substances are strikingly different from either those of homo-polar polymers or simple weak electrolytes.

The prediction of the behavior of polybasic acids from *a priori* considerations is a matter of considerable importance. Maxwell and Partington (4) (5) (6) extend the work of Bjerrum (7) and Gane and Ingold (8) (9) (10) on the ionization constants of dibasic and tribasic acids to acids of any basicity but neglect the energetic interactions between acid groups. The most thorough treatment of polybasic acids to date is to be found in a recent American Chemical Society monograph edited by Cohn and Edsall (11) where a theory is developed for an acid similar to that employed in this study. Cohn and Edsall emphasize the phenomenological interpretation of titration curves of such complex systems as protein solutions whereas this investigation is concerned with a fundamental understanding of the more simple polymeric acids and bases.

Ionization Of Polymeric Electrolytes

By well established methods of statistical mechanics, it can be shown that in a solution of N molecules of an s-basic

acid containing n_{s-i} ions with i protons attached that

$$n_{s-i} = \frac{s!}{(s-i)!\,i!} C_1 X^i Y^{i(i-1)/2} \qquad (1)$$

Here C_1 is a constant which can be determined by requiring that the sum of all n_{s-i} equal N. The parameters X and Y are given by

$$X = \frac{K_o}{(H^+)}$$

$$Y = \exp(-b/kT) \qquad (2)$$

Where K_o is the inherent ionization constant of the acid, (H^+) is the hydrogen ion concentration, and b is the intra-molecular energy of ionization. With these equations it is possible to calculate theoretically the degree of dissociation, α, of the acid in question.

It will be recalled that α is defined as the ratio of the number of protons in a solution to the number which would be there if the acid were completely ionized, thus

$$\alpha = \frac{sn_o + (s-1)n_1 + (s-2)n_2 + \ldots + 2n_{s-2} + n_{s-1}}{Ns} \qquad (3)$$

Since to the first approximation, α is also equal to the ratio of the equivalent conductance at a particular concentration to the limiting equivalent conductance, one can perdict the variation of equivalent conductance with concentration. This makes possible the comparison of the theory with experiment. Data on three polymeric acids show that the theory is compatible with observation.

Partially Neutralized Polymeric Acids

Partially neutralized polymeric acids exhibit properties

which are peculiar to high molecular weight compounds. The intrinsic viscosity changes markedly with both concentration and degree of neutralization. This is due to the uncoiling of the polymeric ions as the charges on them increase. The conductance of solutions of these materials is also interesting. It is found that the measured conductance is much less than that calculated for the small ions, assuming Kohlraush's law of independent migration. This can be attributed to the formation of a partially unionized alkali salt of the polymeric acid. The study of the conductance of partially neutralized solutions allows the estimation of the amount of undissociated alkali. It is found that after half neutralization the association of the metal ions is initiated, and the number of alkali atoms per carboxyl group continues to increase until the ratio is four-tenths near the equivalence point.

The Ionization Constants Of Weak Acids

In connection with the theory on the ionization of polymeric acids it can be shown that the ith dissociation constant of an s-basic acid is given by

$$K_i = \frac{s - i + 1}{i} K_o Y^{i-1} \qquad (4)$$

Maxwell and Partington (6) report the dissociation constants of the carboxylic acids of benzene. If one modifies the general formula of equation (4) to account for ortho, meta, and para electrostatic interactions and calculates the constants of the benzene acids, it is found that these are in excellent agreement with the results of Maxwell and Partington.

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VITA

The author was born in Front Royal, Virginia, on December 23, 1922, and attended the primary and secondary schools of Alexandria, Virginia. After graduating from high school, he entered the George Washington University. The degree of Bachelor of Science in chemistry was awarded him in June, 1943. From that time until February, 1946, when he entered the Graduate College of the University of Illinois, the author was employed by Section H, Division 3, of the National Defense Research Committee to do research on rockets.

He was an Assistant in Chemistry until he was made a special research assistant on the synthetic rubber program of the Office of Rubber Reserve in February, 1947. In September of the same year, he was awarded the Socony-Vacuum Oil Company fellowship in chemistry. The author is a member of the American Chemical Society, Sigma Xi, Phi Lambda Upsilon, and Alpha Chi Sigma.

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